

**R.V. ZAITSEV, M.V. KIRICHENKO, G.S. KHRYPUNOV****CADMIUM SULFIDE THIN FILMS FOR FLEXIBLE SOLAR CELL RECEIVED BY MAGNETRON DISPERSION METHOD**

For the purpose of creation of the economic, suitable for large-scale application technology of formation of a layer of wide-scale "window", for thin-film photo-electric converters on the basis of sulfide and telluride of cadmium the pilot studies of temperature effect of a deposition of the films of sulfide of cadmium received by method of magnetron dispersion on a direct current on their optical properties and crystalline structure were conducted. By method of a two-channel optical spectroscopy it is established that a deposition of films of sulfide of cadmium at a temperature of 160 °C allows to form layers with a width of forbidden region of 1,41 eV that approaches value, characteristic of monocrystals, and the density of the photon flux passing through a cadmium sulfide layer in a spectral interval of a photosensitivity of telluride of cadmium at the level of 37,0 W·nm·cm<sup>2</sup>. Body height of precipitation temperature to 160 °C leads to decrease in optical losses in cadmium sulfide films, as a result of increase in the sizes of areas of a coherent scattering and decrease of level of macrodeformations. At further increase of precipitation temperature up to 230 °C the defining factor leading to growth of optical losses in cadmium sulfide films becomes their impoverishment by an easily volatile component – sulfur.

**Keywords:** cadmium sulfide films, a method of magnetron dispersion on a direct current, optical losses, width of the forbidden region, crystalline structure.

**Р.В. ЗАЙЦЕВ, М.В. КІРІЧЕНКО, Г.С. ХРИПУНОВ****ТОНКІ ПЛІВКИ СУЛЬФІДУ КАДМІЮ ДЛЯ ГНУЧКИХ СОЛЯНИХ ЕЛЕМЕНТІВ, ОТРИМАНІ МЕТОДОМ МАГНЕТРОННОГО РОЗПИЛЕННЯ**

З метою створення економічної, придатної для широкомасштабного застосування технології формування шару широкозонного «вікна» для тонкоплівкових фотоелектричних перетворювачів на основі сульфідів та телуриду кадмію були проведені експериментальні дослідження впливу температури осадження плівок сульфідів кадмію, отриманих методом магнетронного розпилення на постійному струмі, на їх оптичні властивості і кристалічну структуру. Методом двоканальної оптичної спектроскопії встановлено, що осадження плівок сульфідів кадмію при температурі 160 °C дозволяє формувати шари з шириною за-прещеної зони 1,41 eВ, що наближається до значення, характерного для монокристалів, і щільністю потоку фотонів, що проходять через шар сульфідів кадмію в спектральному інтервалі фоточутливості телуриду кадмію, на рівні 37,0 Вт·нм·см<sup>2</sup>.

**Ключові слова:** плівки сульфідів кадмію, метод магнетронного розпилення на постійному струмі, оптичні втрати, ширина забороненої зони, кристалічна структура.

**Р.В. ЗАЙЦЕВ, М.В. КИРИЧЕНКО, Г.С. ХРИПУНОВ****ТОНКИЕ ПЛЕНКИ СУЛЬФИДАКАДМИЯ ДЛЯ ГИБКИХ СОЛНЕЧНЫХ ЭЛЕМЕНТОВ, ПОЛУЧЕННЫЕ МЕТОДОМ МАГНЕТРОННОГО РАСПЫЛЕНИЯ**

С целью создания экономической, пригодной для широкомасштабного применения технологии формирования слоя широкозонного «окна» для тонкопленочных фотоэлектрических преобразователей на основе сульфида и теллурида кадмия были проведены экспериментальные исследования влияния температуры осаждения пленок сульфида кадмия, полученных методом магнетронного распыления на постоянном токе, на их оптические свойства и кристаллическую структуру. Методом двухканальной оптической спектроскопии установлено, что осаждение пленок сульфида кадмия при температуре 160 оС позволяет формировать слои с шириной запрещенной зоны 1,41 эВ, что приближается к значению, характерному для монокристаллов, и плотностью потока фотонов, проходящих через слой сульфида кадмия в спектральном интервале фоточувствительности теллурида кадмия, на уровне 37,0 Вт·нм·см<sup>2</sup>.

**Ключові слова:** плёнки сульфида кадмия, метод магнетронного распыления на постоянном токе, оптические потери, ширина запрещенной зоны, кристаллическая структура.

**Introduction.** In the modern designs of film photo-electric converters (PhEC) on the basis of telluride of cadmium of a back configuration for reduction of speed of the surface recombination of the nonequilibrium charge carriers generated under the influence of light the effect of wide-scale "window" is used [1]. This effect consists areas of the fissile oscillation of nonequilibrium charge carriers from the flawed lit surface by use in a design of PhEC of films the wide-scale of the semiconductor materials possessing a high transmittance in the spectral range corresponding to area of a spectral photosensitivity of a basic layer at a distance. Numerous pilot studies (see, for example, [2, 3]) showed that for film PhEC with a basic layer of telluride of cadmium as wide-scale "window", the optimal solution is use of thin films of sulfide of cadmium. Cadmium sulfide for film PhEC is traditionally made by the following methods: thermal vacuum evaporation, a deposition in selfcontained volume, a chemical deposition and high-pitched magnetron dispersion [4, 5]. CdS films received by these methods have stable vyurttsitny crystalline structure,

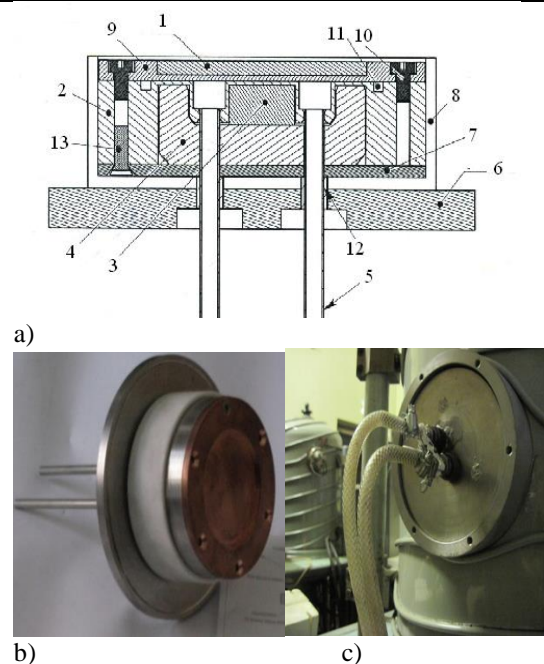
possess a high transmittance in the spectral range corresponding to the range of a photosensitivity of telluride of cadmium are characterized by good adhesion to a layer of the frontal transparent electrode applied on a glass substrate. In a design of the most efficient film PhEC with a basic layer of telluride of cadmium, received by a chemical deposition, CdS films with thickness no more than 100 nanometers are used [6]. However the method of a chemical deposition is problematic to be adapted to conditions of quantity production as it is characterized by low speeds of growthof a film of sulfide of cadmium. At the same time it is necessary to solve issues of regeneration of a fluid chemical wastage. More technological in the conditions of quantity production is the method of thermal vacuum evaporation. However, the conducted researches (see, for example, [7]) showed that thickness of the films of sulfide of cadmium received by this method for use in PhEC on the basis of telluride of cadmium has to be not less than 0,3 microns. Otherwise, owing to through porosity of the films of sulfide of cadmium received by this method which arises owing to

geometrical effect of a shadowing of a surface by the most quickly growing grains a shunting of the separating barrier of instrument structure because of an electrical link of a basic layer of telluride of cadmium to the frontal electrode takes place. The cadmium sulfide films received by method of high-pitched magnetron dispersion are deprived of this shortcoming. However, the large-scale technical application of this method is limited by the high cost of the high-pitched power supply. At the same time, economic, well mastered by domestic electronic industry, the method of not jet magnetron dispersion on a direct current for receiving films of sulfide of cadmium practically is not used.

Thus, the pilot studies of the influence of parameters of magnetron not jet dispersion on a direct current on crystalline structure and optical properties of films of sulfide of cadmium are urgent for creation of the industrial vacuum technologies of receiving of the wide-scale of "windows" for film photo-electric converters with a basic layer of telluride of cadmium of a back configuration.

**Technique of carrying out experiment.** For receiving films of sulfide of cadmium by the method of not jet magnetron dispersion on a direct current [8] developed and made the magnetron adapted to a design of the UVN reference production vacuum installation - 71 - P3 (figure 1). Installation of a magnetron was carried out through a peep-hole of vacuum installation (the figure 1, c).

The design of a magnetron allowed to use target material efficiently. It was caused by the fact that with a diameter of magnetron of 100 mm, diameter of a zone of an erosion made 65 mm, and its width 10 - 12 mm. Such sizes of a zone of an erosion allowed to put films of 70 mm by 70 mm in size with uniformity of thickness at the level of 5%. Therefore, the applied to receiving films, magnetron system can be used in the conditions of the industrial production. Express adaptation allowed to move a substrate together with heating section and the heat-insulating screen in the horizontal plane to such situation at which during preliminary heating pollution of a target was excluded. The target 1 representing the disk with a diameter of 10 cm pressed from cadmium sulfide powder by purity of 99,99% was a source of the sprayed material. The target settled down on a surface of the water-cooled magnetron. In the bottom of the anode of a magnetron there was an input for a tube on which supply of gas mixture of argon and oxygen in spraying system was carried out. The developed design of the radiation heater of a substrate as which glass plates K 8 with thickness of 2 mm thick were used allowed to warm evenly on the area a substrate up to the established temperature in the range of 100 - 220 °C and to maintain temperature with an accuracy of  $\pm$  of 2 °C by means of an automatic regulating system.



1 - target; 2 - housing; 3 - permanent magnet of NdFeB; 4 - magnetic circuit; 5 - cooling tube; 6 - adjusting flange; 7 - cover; 8 - insulator of a housing; 9 - target basis; 10 - screw of fastening of a target (M4x7); 11 - vacuum seal, 12 - the insulator of a tube of cooling, 13 - the screw of fixing of a cover

Fig. 1 – The key diagram (a), photos of a magnetron (b) and installation of magnetron dispersion (c)

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The common pressure of the sprayed gas necessary for operational stability of a magnetron, made 2 Pas. Therefore, between the building bag and the pump the

limitative diaphragm necessary for stable work of a vacuum vapor-steam pump at such low pressure was established. The distance from a substrate to a target which made 35 mm, was defined as minimum at which inhomogeneity of the received film on thickness taking into account a geometrical factor was not exceeded by 5%.

Crystalline structure and phase structure of films were investigated on a X-ray diffractometer the DRON-4M in monochromatic Co-K $\alpha$  radiation. Identification of phases in models was carried out on the basis of comparison of set of the interplanar distances calculated by Woolf - Bragg's formula [9], with the available sets of interplanar distances for tin oxides from the help ASTM cards. Roughing-out of the diffraction peaks was carried out by means of the developed computer program. Such computing machining allowed to define the position of the diffraction peak ( $2\theta$ ), interplanar distance ( $d$ ) and integral intensity ( $I$ ).

Spectral dependences of the coefficients of transmittances and reflection of films of sulfide of cadmium investigated by method of a two-channel optical spectroscopy by means of a spectrophotometer SPh-2000, equipped with the SPhO prefix - 2000 for measurement of reflecting and diffuse reflections. Optical width of the forbidden region of  $E_g$  layers of CdS defined similarly described in [9], by means of extrapolation on an axis of energies of the line section, dependence  $[-\ln(T) \cdot hv]^2$  from  $hv$ .

Results and their discussion.

**1. Research of optical properties of films of sulfide of cadmium.** Films of sulfide of cadmium were received by method of magnetron dispersion on a direct current with a pressure of working gas of 0,9 - 1 Pa, 550 - 600 V tension category and current densities 0,44 - 0,53 mA/cm<sup>2</sup>. At the same time precipitation temperature varied from 100 °C to 230 °C. Such ranges of parameters of the technological modes can be considered suitable for procreation in the production conditions. Time of a deposition of films made 5 minutes.

The research of optical properties of films of sulfide of cadmium was conducted by means of measurements of spectral dependences of transmittances and reflection of films of CdS in the spectral range of 400 - 1100 nanometers (figure 2). The analysis of transmission spectrums shows that for all models, except the model received at precipitation temperature of 100 °C the strong absorption in the range of lengths of waves of 400 - 500 nanometers and a sharp edge of an absorption band in the range of 500 - 550 nanometers is observed. At the same time in red and infrared spectral ranges a high transparency at the level of 80% is observed.

Analytical processing of transmission spectrums and reflection allowed to determine optical parameters of the studied films received at various precipitation temperatures.

In the figure 3 results of definition of width of the forbidden region ( $E_g$ , eV) and values of theoretical power of a luminous flux ( $W$ , Wt·nanometer·cm<sup>2</sup>) which can pass through the studied cadmium sulfide films in the conditions of illumination of AM 1,5, in a spectral interval of a photosensitivity of PhEC on the basis of

sulfide and telluride of cadmium which, according to literary data [8], makes 550 - 900 nanometers are given. These two parameters determine the size of optical losses in a cadmium sulfide layer at its use as wide-scale "window" in film photo-electric converters with a basic layer of telluride of cadmium of a back configuration. Optical researches showed that with growth of precipitation temperature to 160° C there is an increase, passed from through a film of sulfide of cadmium, power of a luminous flux 32,7 W·nm·cm<sup>2</sup> to 37 W·nm·cm<sup>2</sup>. Further growth of precipitation temperature to 230 °C leads to decrease in last power of a luminous flux to 33,5 Wt·nanometer·cm<sup>2</sup>. The analysis of the figure 3 demonstrates that with growth of precipitation temperature from 100 °C to 160 °C there is an increase in width of the forbidden region from 2,38 eV to 2,41 eV.

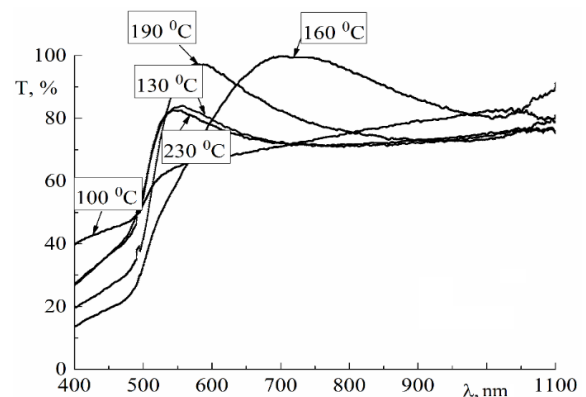


Fig. 2 – Spectral dependences of the coefficients of transmittances of the films of sulfide of cadmium received at various precipitation temperatures

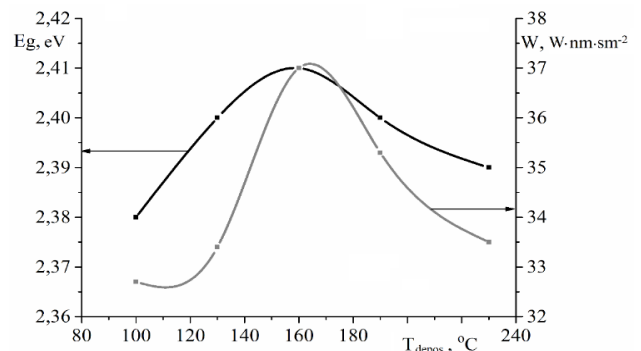


Fig. 3 - Optical parameters of films of CdS received by the method of magnetron dispersion

Further growth of precipitation temperature from 160° C to 230° C leads to decrease in width of the forbidden region from 2,41 eV to 2,39 eV. According to literary data [4] for monocrystal films of sulfide of cadmium width of the forbidden region makes 2,42 - 2,45 eV. Smaller values of width of the forbidden region for polycrystalline films of sulfide of cadmium, in comparison with monocrystals, are caused by the fact that borders of grains absorb light as metal layers that leads to decrease in size of the forbidden region determined by optical techniques. Except a developed grainbordered surface decrease in optical width of the forbidden region



can be caused by impoverishment of films of sulfide of cadmium by easily volatile component – sulfur.

Thus, for use in a design of high performance PhEC on the basis of sulfide and telluride of cadmium it is necessary to use the films received at precipitation temperature of 160 °C as at the same time the maximal stream density fluence of the photons coming to a basic layer of telluride of cadmium that allows to increase the coefficient of efficiency due to growth of a current density of a short-circuit.

**2. Research of crystalline structure and element structure of films of sulfide of cadmium.** For identification of the physical mechanisms defining dependence of width of the forbidden region of the films of sulfide of cadmium received by magnetron dispersion on a direct current researches of crystalline structure of films were conducted by method of a x-ray diffractometry (figure 4). On the experimental roentgendifraktogrammas only one peak on angle  $2\theta = 30,62^\circ$  which corresponds to reflection (111) cubic modification or to reflection (002) of the hexagonal phase CdS which are theoretically characterized by the maximal intensity is observed. Because of the small thickness of a model other diffraction peaks were not identified that does not allow to uniquely determinate phase structure of the received CdS models by a roentgendifraktometrical method. Nevertheless, in view of the fact that stable modification of CdS is hexagonal, further processing investigated roentgendifraktogramm was carried out for the hexagonal phase CdS. Results of analytical processing of structural researches are presented in table 1.

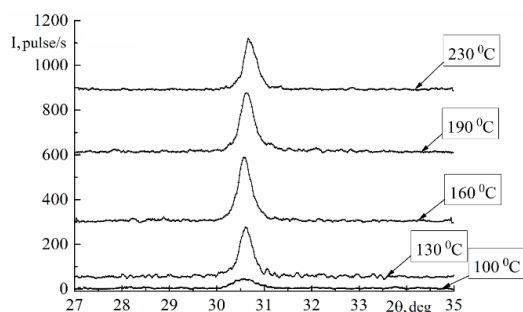


Fig. 4 – Roentgendifraktogramma of the films of sulfide of cadmium received by method of magnetron dispersion on a direct current at various precipitation temperatures

With growth of precipitation temperature from 100 °C to 230 °C decrease in interplanar distance (002) from  $d_{002} = 3,391 \text{ \AA}$  to  $d_{002} = 3,379 \text{ \AA}$  is observed, that corresponds to decrease in parameter from a hexagonal lattice from  $c = 6,782 \text{ \AA}$  to  $c = 6,758 \text{ \AA}$ . The received values of parameter  $c$  is more than table value, what is characteristic for monocrystals ( $c = 6,7198 \text{ \AA}$ ). It demonstrates existence of the squeezing macrovoltage which size decreases with increase of temperature up to 230 °C. With increase of precipitation temperature from 100 °C to 230 °C decrease of a physical broadening of the diffraction peak from  $\Delta\theta = 0,38^\circ$  to  $\Delta\theta = 0,30^\circ$  is observed. The assessment on the specified width of the diffraction peaks shows that with increase of precipitation

temperature growth of areas of a coherent scattering from 25,2 nanometers to 31,9 nanometers is observed. Thus, with increase of precipitation temperature from 100 °C to 230 °C natural increase in quality of crystalline structure of films of sulfide of cadmium is observed: decrease in level of macrovoltages and increase in the sizes of areas of a coherent scattering is observed that reduces light absorption on a developed grainbordered surface. Decrease in level of microdeformation and growth of the sizes of areas of a coherent scattering cause growth of optical width of the forbidden region.

Table 1 – Results of analytical processing of structural researches of films of CdS received by method of magnetron dispersion on a direct current

No	Precipitation temperature, °C	Position of peak, degree	Inter-planar distance ( $d_{002}$ ), Å	Half-width of the diffraction peak ( $\Delta\theta$ ), degree	L, nm
1	100	30,58	3,391	0,38	25,2
2	130	30,62	3,388	0,33	29,0
3	160	30,59	3,391	0,33	29,0
6	190	30,64	3,385	0,34	28,1
5	230	30,70	3,379	0,30	31,9

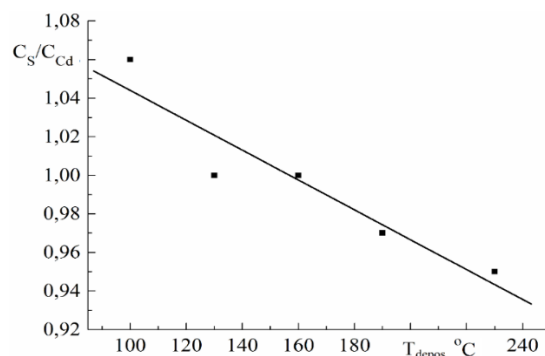


Fig 5 – The relation of atomic concentration of sulfur and cadmium of the films of sulfide of cadmium received by method of magnetron dispersion on a direct current at various precipitation temperatures

Researches of crystalline structure were added with researches of elemental structure of the received films which were conducted on a spectrometer Elvatech of the Elvate company. Time of set of impulses made 240 - 241 second. Researches showed (figure 5) that with increase of precipitation temperature from 100 °C to 230 °C the attitude of atomic concentration of sulfur ( $C_s$ ) towards atomic concentration of cadmium ( $C_{Cd}$ ) decreases from  $C_s/C_{Cd} = 1,06$  to  $C_s/C_{Cd} = 0,95$  that is bound to impoverishment of the growing film an easily volatile component which sulfur is.

Thus, with increasing of precipitation temperature decrease in degree of stoichiometry of films that is caused by increasing of a vacancies concentration, causing growth of light absorption and decrease of efficient optical width of the forbidden region, as a result of emergence in the forbidden region of the energy levels capable to share

in the transition of charge carriers activated by light is observed.

**Conclusions.** For use in a design of film photoelectric converters of a back configuration with a basic layer of telluride of cadmium optimum precipitation temperature of films of sulfide of cadmium by method of not jet magnetron dispersion on a direct current makes 160 °C that is caused by achievement of the greatest width of the forbidden region -1,41 eV and the maximal flux density of the photons arriving through a cadmium sulfide layer in the spectral range of a photosensitivity of telluride of cadmium. The extremum on dependence of optical properties of the studied cadmium sulfide films from precipitation temperature is caused by existence of two competing physical mechanisms. Body height of precipitation temperature to 160 °C leads to decrease in optical losses in cadmium sulfide films, as a result of increase in the sizes of areas of a coherent scattering and decrease of level of macrodeformations. At further increase of precipitation temperature up to 230 °C the defining factor leading to growth of optical losses in cadmium sulfide films becomes their impoverishment by an easily volatile component – sulfur.

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